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UNITED STATES PATENT APPLICATION

OF

FLORENCE LAURENT AND ROLAND DE LA METTRIE

FOR

**OXIDATION DYEING PROCESS AND OXIDATION DYE
COMPOSITION FOR KERATIN FIBRES WHICH COMPRISES A
CATIONIC AMPHIPHILIC POLYMER**

The invention relates to an oxidation dyeing process for keratin fibres, and in particular human keratin fibres such as the hair, with compositions comprising, in a medium which is suitable for dyeing, at least one oxidation dye precursor, optionally one or more couplers, at least one oxidizing agent and at least one cationic amphiphilic polymer.

It is a well known practice to dye keratin fibres, and in particular the hair, with dye compositions containing oxidation dye precursors, which are generally referred to as "oxidation bases", in particular ortho- or para-phenylenediamines, ortho- or para-aminophenols and heterocyclic bases.

Oxidation dye precursors are compounds which are initially colourless or only weakly coloured, and which develop their dyeing power on the hair in the presence of an oxidizing agent. The formation of the coloured compounds results either from a condensation of the "oxidation bases" with themselves or from a condensation of the "oxidation bases" with coloration modifier compounds, or "couplers", which are generally present in the dye compositions used in oxidation dyeing and which are represented more particularly by meta-phenylenediamines, meta-aminophenols and meta-diphenols and certain heterocyclic compounds.

The variety of molecules used, which consist of the "oxidation bases", and of the "couplers", allows a wide variety of colours to be obtained.

During application of the coloration product onto the hair, it is necessary to keep

this product on the application area and to prevent it from running onto the face or outside the zones which it is desired to dye. For this, use has been made of traditional thickeners such as crosslinked poly(acrylic acid), hydroxyethylcelluloses, waxes or even certain nonionic surfactants which, when suitably chosen, give rise to a thickening effect, or even a gelling effect, of aqueous media.

However, the inventors have observed that the ingredients of the traditional thickener type, surfactants and solvents, generally halt the rise of the dye on the fibres, which is reflected in less luminous shades. In order to obtain equivalent chromaticity, it is then necessary to use larger amounts of dyes as well as more solvent and/or more surfactants to dissolve these dyes.

The inventors have also found that compositions containing the oxidation dye precursor(s) and, optionally, the coupler(s), and thickened with traditional thickeners, lose some of their gelled nature when they are mixed with the composition containing the oxidizing agent.

After extensive research conducted in this field, the inventors have discovered that introducing an effective amount of a specific cationic associative polymer, as thickener,

(i) either into the composition containing the oxidation dye precursor(s) and, optionally, the coupler(s) (Composition A),

(ii) or into the oxidizing composition (Composition B),

(iii) or into the two compositions (A and B) at the same time,

gives oxidation dye compositions which, even after mixing with the oxidizing agent, do not run and consequently remain better localized at the point of application. These

5 compositions, moreover, give rise to more chromatic (more luminous) shades and more intense shades than do equivalent compositions containing usual thickener systems.

The colorations obtained moreover have good resistance to perspiration.

For the purposes of the invention, the chromaticity (luminosity) is defined by the value C^* in the L^* , a^* , b^* colorimetric notation system of the Commission Internationale
10 de l'Éclairage (C.I.E.) [International Commission on Illumination]. This value is equal to the square root of the sum $a^2 + b^2$ (+a is red, -a is green, +b is yellow, -b is blue). A shade is proportionately more luminous the larger the value of C^* . In this notation system, L^* defines the intensity of the shade. The shade is proportionately more intense the lower the value of L^* (0 = black, 100 = white).

15 By means of the invention, it is also possible to advantageously reduce, or even dispense with altogether, the use of surfactants.

The invention also makes it possible to reduce the amount of colouring active materials used in the dye compositions when compared with the conventional and known techniques of the prior art.

According to the invention, the term "associative polymers" means water-soluble polymers capable, in an aqueous medium, of reversibly *combining* with each other or with other molecules. The chemical structure of these polymers, also known as "amphiphilic polymers", is characterized by the presence of hydrophilic zones which provide the water-solubility, and of hydrophobic zones by which the polymers, in an aqueous medium, assemble with each other or with the hydrophobic parts of other molecules.

One subject of the invention is thus a process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, which comprises applying to the fibres an oxidation dye composition (A) containing, in a medium which is suitable for dyeing, at least one oxidation dye precursor and optionally one or more couplers, and in developing the colour in alkaline, neutral or acidic medium using an oxidizing composition (B) containing an oxidizing agent, at least one of the compositions (A) and (B) also containing an effective amount of at least one cationic amphiphilic polymer chosen from:

- quaternized celluloses modified with groups containing at least one fatty chain selected from alkyl, arylalkyl and alkylaryl groups, preferably containing at least 8 carbon atoms, more preferably 8 to 30 carbon atoms, which, of course, includes mixtures thereof, and

- quaternized hydroxyethylcelluloses modified with groups containing at least one fatty chain selected from alkyl, arylalkyl and alkylaryl groups, preferably containing at least 8 carbon atoms, more preferably 8 to 30 carbon atoms, which, of course, includes mixtures thereof,

5 preferably the compositions (A) and (B) being mixed together immediately before use or applied one after the other to the keratin fibres.

Another subject of the invention is also an oxidation dye composition for keratin fibres, in particular for human keratin fibres, which comprises, in a medium which is suitable for dyeing, at least one oxidation dye precursor, where appropriate, one or
10 more couplers and at least one cationic amphiphilic polymer chosen from:

- quaternized celluloses modified with groups containing at least one fatty chain selected from alkyl, arylalkyl and alkylaryl groups, preferably containing at least 8 carbon atoms, which, of course, includes mixtures thereof, and

- quaternized hydroxyethylcelluloses modified with groups containing at least one
15 fatty chain selected from alkyl, arylalkyl and alkylaryl groups, preferably containing at least 8 carbon atoms, which, of course, includes mixtures thereof.

Another subject of the invention is an oxidizing composition which is used to develop the colour of an oxidation dye composition and comprising at least one oxidizing agent and at least one cationic amphiphilic polymer as defined above.

Yet another subject of the invention is a ready-to-use composition for dyeing keratin fibres, which contains at least one oxidation dye precursor, optionally one or more couplers, at least one cationic amphiphilic polymer as defined above and at least one oxidizing agent.

5 Another subject of the invention includes multi-compartment dyeing devices or dyeing kits containing at least two compartments, one of which contains a composition (A) comprising, in a medium which is suitable for dyeing, at least one oxidation dye precursor and optionally one or more couplers, and another compartment contains an oxidizing composition (B) comprising at least one oxidizing agent, at least one of the
10 compositions (A) and (B) also comprising an effective amount of at least one cationic amphiphilic polymer as defined above.

 The alkyl radicals borne by the above quaternized celluloses or hydroxyethylcelluloses preferably contain from 8 to 30 carbon atoms, more preferably 12 to 18 carbon atoms. The aryl radicals are preferably phenyl, benzyl, naphthyl or
15 anthryl groups.

 Representative quaternized alkylhydroxyethylcelluloses containing C₈₋₃₀ fatty chains include the products Quatrisoft LM 200, Quatrisoft LM-X-529-18-A, Quatrisoft LM-X-529-18B (C₁₂ alkyl) and Quatrisoft LM-X 529-8 (C₁₈ alkyl) sold by the company Amerchol and the products Crodacel QM, Crodacel QL (C₁₂ alkyl) and Crodacel QS (C₁₈

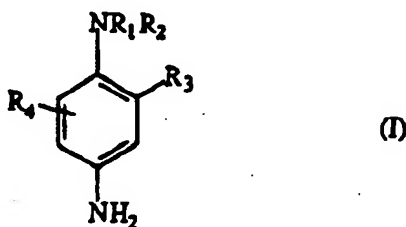
alkyl) sold by the company Croda.

The cationic amphiphilic polymers used in the compositions of the present invention are preferably present in an amount ranging from 0.05 to 10% by weight, more preferably in an amount ranging from 0.1 to 5% by weight, even more preferably from 0.1 to 0.2%, relative to the weight of the oxidation dye composition (A) or of the oxidizing composition (B).

The oxidation dye precursors which can be used in the context of the present invention are chosen from those conventionally known in oxidation dyeing.

Representative oxidation dye precursors include:

- the para-phenylenediamines of formula (I) below, and the acid addition salts thereof



in which

R_1 represents a hydrogen atom or a C_{1-4} alkyl radical, a C_{1-4} monohydroxyalkyl

radical, a C₂₋₄ polyhydroxyalkyl radical or a 4'-aminophenyl radical,

R₂ represents a hydrogen atom or a C₁₋₄ alkyl radical, a C₁₋₄ monohydroxyalkyl radical or a C₂₋₄ polyhydroxyalkyl radical,

R₃ represents a hydrogen atom, a halogen atom such as a chlorine atom, or a C₁₋₄ alkyl radical, a sulphy radical, a carboxyl radical, a C₁₋₄ monohydroxyalkyl radical or a C₁₋₄ hydroxyalkoxy radical,

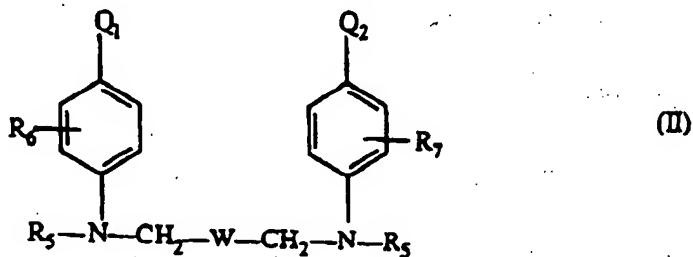
R₄ represents a hydrogen atom or a C₁₋₄ alkyl radical.

Preferred para-phenylenediamines of formula (I) above are, for example para-phenylenediamine, para-toluylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 4-amino-N,N-bis(β-hydroxyethyl)-3-methylaniline, 4-amino-3-chloro-N,N-bis(β-hydroxyethyl)aniline, 2-β-hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylene, N-(β-hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N-ethyl-N-(β-hydroxyethyl)-para-phenylenediamine, N-(β, γ-dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine,

N-phenyl-para-phenylenediamine and 2- β -hydroxyethyloxy-para-phenylenediamine, and the acid addition salts thereof.

Among the para-phenylenediamines of formula (I) above, the ones most particularly preferred are para-phenylenediamine, para-toluylenediamine, 2-isopropyl-
 5 para-phenylenediamine, 2- β -hydroxyethyl-para-phenylenediamine, 2- β -hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis-(β -hydroxyethyl)-para-phenylenediamine and 2-chloro-para-phenylenediamine, and the acid addition salts thereof.

10 - the bis(phenyl)alkylenediamines of formula (II):



in which

- Q_1 and Q_2 , which may be identical or different, represent a hydroxyl radical or a NHR_8 radical in which R_8 represents a hydrogen atom or a C_{1-4} alkyl radical,

R_5 represents a hydrogen atom or a C_{1-4} alkyl radical, a C_{1-4} monohydroxyalkyl radical, a C_{2-4} polyhydroxyalkyl radical or a C_{1-4} aminoalkyl radical in which the amino group may be substituted,

R_6 and R_7 , which may be identical or different, represent a hydrogen or a halogen atom or a C_{1-4} alkyl radical,

W represents a radical chosen from the group formed by the following radicals:

$-(CH_2)_n-$; $-(CH_2)_m-O-(CH_2)_m-$; $-(CH_2)_m-CHOH-(CH_2)_m-$ and

$-(CH_2)_m-N(CH_3)-(CH_2)_m-$;

in which n is an integer from 0 to 8 and m is an integer from 0 to 4, and the acid

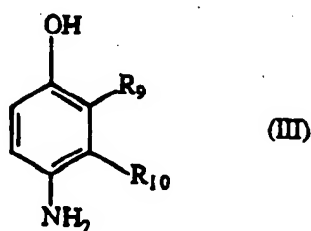
addition salts thereof.

Representative bis(phenyl)alkylenediamines of formula (II) above include N,N' -bis(β -hydroxyethyl)- N,N' -bis(4-aminophenyl)-1,3-diamino-2-propanol, N,N' -bis(β -hydroxyethyl)- N,N' -bis(4-aminophenyl)ethylenediamine, N,N' -bis(4-aminophenyl)tetramethylenediamine, N,N' -bis(β -hydroxyethyl)- N,N' -bis(4-aminophenyl)tetramethylenediamine, N,N' -bis(4-methylaminophenyl)tetramethylenediamine, N,N' -bis(β -hydroxyethyl)- N,N' -bis(4-aminophenyl)tetramethylenediamine and N,N' -bis(ethyl)- N,N' -bis(4-amino-3-methylphenyl)ethylenediamine, and the acid addition salts thereof.

A preferred bis(phenyl)alkylenediamine of formula (II) is N,N' -bis(β -hydroxyethyl)- N,N' -bis(4'-aminophenyl)-1,3-diamino-2-propanol, or one of the acid addition salts

thereof.

- the para-aminophenols corresponding to formula (III):



in which

5 R_9 represents a hydrogen atom or a C_{1-4} alkyl radical, a C_{1-4} monohydroxyalkyl radical, a (C_{1-4}) alkoxy (C_{1-4}) alkyl radical or a C_{1-4} aminoalkyl radical, or a hydroxy (C_{1-4}) alkylamino (C_{1-4}) alkyl radical;

10 R_{10} represents a hydrogen or fluorine atom or a C_{1-4} alkyl radical, a C_{1-4} monohydroxyalkyl radical, a C_{2-4} polyhydroxyalkyl radical, a C_{1-4} aminoalkyl radical, a cyano (C_{1-4}) alkyl radical or a (C_{1-4}) alkoxy (C_{1-4}) alkyl radical, and the acid addition salts thereof, with the proviso that at least one of the radicals R_9 or R_{10} represents a hydrogen atom.

-Preferred para-aminophenols of formula (III) above include para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol and 4-amino-2-(β -hydroxyethylaminomethyl)phenol, and the acid addition salts thereof.

- the ortho-aminophenols which can be used as oxidation bases in the context of the invention are chosen in particular from 2-aminophenol, 2-amino-1-hydroxy-5-methylbenzene, 2-amino-1-hydroxy-6-methylbenzene and 5-acetamido-2-aminophenol, and the acid addition salts thereof;

- the heterocyclic bases which can be used as oxidation bases in the context of the invention are chosen in particular from pyridine derivatives, pyrimidine derivatives and pyrazole derivatives, and the acid addition salts thereof.

Preferred pyridine derivatives include the compounds described, for example, in patents GB-1,026,978 and GB-1,153,196, specifically incorporated by reference herein, such as 2,5-diaminopyridine, and the acid addition salts thereof.

Preferred pyrimidine derivatives include the compounds described, for example, in German patent DE-2,359,399 or Japanese patents JP-88-169,571 and JP-91-333,495, specifically incorporated by reference herein, such as 2,4,5,6-tetraaminopyrimidine and 4-hydroxy-2,5,6-triaminopyrimidine, and the acid addition salts thereof.

Preferred pyrazole derivatives include the compounds described in patents DE-3,843,892, DE-4,133,957 and patent applications WO-94/08969 and WO-94/08970, specifically incorporated by reference herein, such as 4,5-diamino-1-methylpyrazole, 3,4-diaminopyrazole and 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, and the acid addition salts thereof.

According to the invention, the oxidation dye precursor(s) preferably is present in an amount ranging from 0.0005 to 12% by weight relative to the total weight of the composition (A) and more preferably from 0.005 to 6% by weight of the total weight of the composition approximately.

The couplers which can be used in the dyeing process according to the invention are those conventionally used in oxidation dye compositions, i.e. meta-phenylenediamines, meta-aminophenols and meta-diphenols (resorcinols), mono- or polyhydroxylated naphthalene derivatives, sesamol and its derivatives and heterocyclic compounds such as, for example, indole couplers, indoline couplers and pyridine couplers, and the acid addition salts thereof.

These couplers may be chosen in particular from 2-methyl-5-aminophenol, 5-N-(β -hydroxyethyl)amino-2-methylphenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 1-(β -hydroxyethoxy)-2,4-diaminobenzene, 2-amino-4-(β -hydroxyethylamino)-1-methoxybenzene, 1,3-

diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane, sesamol, α -naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 6-hydroxyindoline, 2,6-dihydroxy-4-methylpyridine, 1-H-3-methylpyrazol-5-one and 1-phenyl-3-methylpyrazol-5-one, and the acid addition salts thereof.

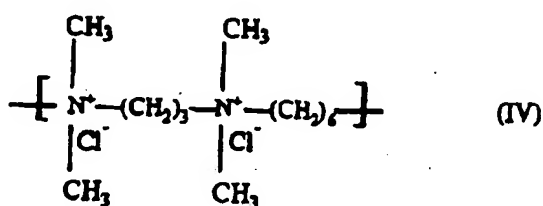
5 When they are present, these couplers preferably are represent in an amount ranging from about 0.0001 to about 10% by weight relative to the total weight of the composition (A), and in particular from about 0.005 to about 5% by weight of the composition (A).

10 In general, the acid addition salts thereof the chromogenic compounds, i.e. the oxidation bases and the couplers, are chosen in particular from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

15 In addition to the oxidation dye precursors defined above and the optional associated couplers, the composition (A) may contain direct dyes in order to enrich the shades with glints. These direct dyes may be chosen in particular from nitro dyes, azo dyes and anthraquinone dyes.

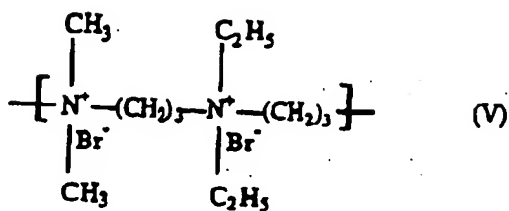
 The composition (A) and/or the composition (B) may also contain at least one cationic or amphoteric substantive polymer such as those defined in EP-A-0,673,641, specifically incorporated by reference herein, among which it is advantageously preferred to use:

- the poly(quaternary ammonium) polymers prepared and described in French patent 2,270,846, specifically incorporated by reference herein, containing repeating units corresponding to formula (IV) below:



5 and particularly those whose weight-average molar mass, determined by gel permeation chromatography, is from 9500 to 9900;

- the poly(quaternary ammonium) polymers prepared and described in French patent 2,270,846, specifically incorporated by reference herein, containing repeating units corresponding to formula (V) below:



and particularly those whose weight-average molar mass, determined by gel permeation chromatography, is about 1200.

The medium for the composition (A) which is suitable for dyeing is preferably an aqueous medium consisting mainly of water and optionally containing cosmetically acceptable organic solvents, among which are alcohols such as ethyl alcohol, isopropyl alcohol, benzyl alcohol and phenylethyl alcohol; glycols or glycol ethers such as ethylene glycol monomethyl, monoethyl and monobutyl ethers, propylene glycol or its ethers, such as propylene glycol monomethyl ether; butylene glycol; dipropylene glycol and diethylene glycol alkyl ethers such as, for example, diethylene glycol monomethyl or monobutyl ether, in concentrations ranging from about 0.5 to about 20% by weight, and preferably from about 2 to about 10% by weight, relative to the total weight of the composition.

The composition (A) and/or the composition (B) may also contain an effective amount of other agents commonly used in the cosmetics field. These adjuvants are, for example, sequestering agents, hair conditioners and in particular silicones, preserving agents, opacifiers, etc., and optionally anionic, nonionic or amphoteric surfactants, or mixtures thereof.

The said dye composition may also contain antioxidants. These can be chosen in particular from sodium sulphite, thioglycolic acid, thiolactic acid, sodium bisulphite, dehydroascorbic acid, hydroquinone, 2-methylhydroquinone, tert-butylhydroquinone and homogentisic acid. They are present, where appropriate, in an amount ranging from about 0.05 to about 3.0% by weight relative to the total weight of the composition.

Needless to say, a person skilled in the art will take care to select the optional complementary compound(s) mentioned above, such that the advantageous properties intrinsically associated with the dye composition according to the invention are not, or are virtually not, adversely affected by the addition(s) envisaged.

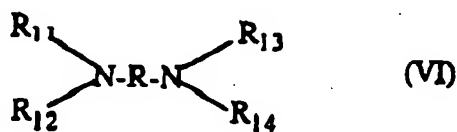
In the composition (B), the oxidizing agent is preferably chosen from hydrogen peroxide, urea peroxide, alkali metal bromates or ferricyanides, and salts of peracids such as perborates, percarbonates and persulphates. It is preferred in particular to use hydrogen peroxide.

The composition (B) advantageously comprises an aqueous hydrogen peroxide

solution whose titre preferably ranges from about 2.5 to about 40 volumes, in particular from about 5 to about 20 volumes.

The value of the pH of the ready-to-use composition, resulting from mixing the dye composition (A) and the oxidizing composition (B), generally ranges from 4 to 11, and preferably from 6 to 10.5. It can be adjusted using acidifying or basifying agents which are well known in the art of oxidation dyeing of keratin fibres.

Among the basifying agents which may be used, for example, are aqueous ammonia, alkali metal carbonates, alkanolamines such as mono-, di- and triethanolamine and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (VI) below:



in which R is a propylene residue optionally substituted with a hydroxyl group or a C₁₋₄ alkyl radical; R₁₁, R₁₂, R₁₃ and R₁₄, which may be identical or different, represent a hydrogen atom or a C₁₋₄ alkyl radical or a C₁₋₄ hydroxyalkyl radical.

The acidifying agents are conventionally, for example, inorganic or organic acids such as hydrochloric acid, orthophosphoric acid, carboxylic acids such as tartaric acid, citric acid or lactic acid, or sulphonic acids.

5 The dyeing process according to the invention preferably comprises applying a mixture, prepared extemporaneously at the time of use from the compositions (A) and (B) described above, to the wet or dry keratin fibres, and in leaving this mixture to act for an exposure time preferably ranging from 1 to 60 minutes approximately, and more particularly from 10 to 45 minutes approximately, rinsing the fibres, then optionally washing them with shampoo and rinsing them again and drying them.

10 It is clearly understood that the preceding description has been given purely for non-limiting illustrative purposes and that variants or modifications may be made thereto in the context of the present invention.

Examples illustrating the invention will now be given, without, however, being limiting in nature.

Example

The following oxidation dye composition is prepared:

	oxyethylenated (3) decyl alcohol	9%
	oleyl alcohol	6%
5	oleic acid	3%
	alkylpolyglycoside (1.4)	6.9%
	ethyl alcohol	6.5%
	ethylene glycol monobutyl ether	10%
	quaternized laurylhydroxyethylcellulose	
10	(sold under the name Quatrisoft LM 200 by the company Amerchol)	0.2%
	sequestering agent	qs
	reducing agent	qs
	fragrance	qs
15	antioxidant	qs
	20% aqueous ammonia	10%
	1,3-dihydroxybenzene	0.4%
	3-aminophenol	0.074%

	1-(β -hydroxyethoxy)-2,4-diaminobenzene	
	dihydrochloride	0.0094%
	1,3-dihydroxy-2-methylbenzene	0.15%,
	N,N'-bis(β -hydroxyethyl)-N,N'-bis-	
5	(4-aminophenyl)-1,3-diamino-2-propanol	
	tetrahydrochloride	0.1%
	para-phenylenediamine	0.63%
	demineralized water	qs 100%

10 The above dye composition is mixed, at the time of use, weight for weight with a 20-volumes hydrogen peroxide solution (6% by weight).

The mixture obtained is applied to locks of natural grey hair containing 90% white hairs, for 30 minutes. The locks are then rinsed, washed with a standard shampoo, rinsed again and then dried.

A light-chestnut shade is obtained.